

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
APPLICATION FOR U.S. LETTERS PATENT

Title:

LOW FRICTION PLANARIZING/POLISHING PADS AND USE THEREOF

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TITLE OF INVENTION  
LOW FRICTION PLANARIZING/POLISHING PADS AND USE THEREOF

TECHNICAL FIELD

The present invention relates to pads and use thereof. The pads are especially useful for planarizing and polishing surfaces in the microelectronics industry. More particularly the present invention relates to increasing the topological selectivity of planarizing/polishing pads by providing pads containing a polymeric matrix and solid lubricant particles. An added advantage of the pads of the present invention is that the reduced friction between the pads and surface being planarized/polished e.g.-wafer reduces delamination (peeling) due to planarization/polishing, which is particularly important in planarizing conductor lines embedded in low-k (i.e. low dielectric constant) insulators or porous low-k insulators or planarizing the insulators themselves. Furthermore, such pads reduce defects such as scratches.

BACKGROUND OF THE INVENTION

In microelectronics planarization metal or insulator layers are deposited conformally into etched trenches of a substrate after which a need exists to planarize the surface with chemical mechanical planarization (CMP). With device dimensions becoming smaller and smaller involving not only narrower conductor and insulator lines but also thinner and thinner layers both in front- end, and back- end of the line applications, post CMP specifications for permissible deviation from perfect planarity are becoming tighter. The deviation from perfect planarity, referred to as a step, is detrimental due to depth-of-focus issues in subsequent lithography steps. Also, this deviation in the case of oxide polish can lead to field threshold problems in isolation regions, while in the case of metal planarization can cause shorts in the next metal level. For devices manufactured in the near future it is important to achieve a post-planarization step-height of less than 100 Angstroms on a 100 microns x 100 microns test site.

For example, a shallow trench isolation (STI) structure is shown in Figure 1a before planarization. In order to achieve perfect planarization, a CMP process is required which has a high degree of topological selectivity meaning that it removes material from the “up” areas of the wafer, but it does not remove material from the “down” areas of the wafer until the level of the up area reaches the level of the down area as shown in Figure 1b. If material is removed from the down area before it becomes level with the up area, “dishing” results i.e. a post CMP step will remain as shown in Figure 1b’.

It is well known that when the pad and wafer are separated by the slurry layer known as hydrodynamic polishing, shown in Figure 2a, removal rates are small. Significant polish rates result only when the planarizing pad is in contact with the wafer. Most importantly significant removal rates in the down area take place only when the down area is in contact with the pad as shown in Figure 2b.

The present inventor has determined the mechanism believed responsible for the polishing pad extending into the down area of the wafer. In particular, the inventor of this application discovered that the most commonly used prior art polishing pad, the IC1000 pad, which is a foam polyurethane from Rodel Corporation develops normal stresses in the direction perpendicular to the plane of the pad when submitted to a surface torque. The normal stress is a linear function of the square of the torque. This normal stress creates an extension of the pad into the down areas of the wafer, and consequently promotes dishing.

While the pad exhibits this phenomenon when tested in the dry condition, when a slurry is applied, the torque, which represents friction, increases and so, does the normal force and the pad extension into the down areas of the wafer.

The present inventor’s U.S. Patent Serial No. 10/295/836, filed November 18, 2002 and entitled “Polishing Compositions and Use Thereof” discloses, inter alia, planarizing slurries with reduced friction by adding organic solid lubricant particles such as poly (tetrafluoroethylene) (PTFE) to the slurry containing the abrasive. The disclosure of USSN 10/295,836 is incorporated herein by reference.

The solid lubricant additive reduced the torque i.e. friction between pad and wafer and eliminated the normal force, thus the extension of the pad into the down areas of the wafer, consequently it reduced dishing and provided for improved planarization.

Nevertheless, room for improvement exists. For instance, some dishing can still occur probably due to the hydrodynamic component of the planarizing process and that component was increased from adding the PTFE dispersion, the preferred solid lubricant, to the abrasive slurry, most likely from the additives used to disperse the PTFE particles. This can be counteracted by increasing the overfill of the material to be planarized (overfill is film thickness minus etched step-height as illustrated in Figure 1), but this is not an advantage. Another obstacle of using solid lubricant particles in the slurry is that due to the chemical inertness of PTFE, it is not easy to create a hydrophilic dispersion to be used with water-base abrasive slurries. Consequently only a very limited number of vendors commercially offer such dispersions.

Also, as discussed above, reducing friction between pad and wafer is important in addition to improved planarization in reducing surface damage created during planarization, such as peeling and scratches, particularly in planarizing conductors over low-k dielectric insulators or the low-k dielectric insulators themselves. The current approach is to use very low down force to reduce friction which results in non-economical removal rates.

## SUMMARY OF THE INVENTION

The present invention provides for improving the topological selectivity of the polymeric planarizing/ polishing pads by providing pads comprising a polymeric matrix and solid lubricant particles. This is achievable by the present invention without a need to alter the polymer matrix, the manufacturing process or surface micro or macro texture of prior art polishing pads.

More particularly, an aspect of the present invention relates to a pad comprising a polymeric matrix and solid lubricant particles. The solid lubricant particles are typically present in amounts of about 0.5% to about 30% weight of the pad.

Another aspect of the present invention relates to a method for polishing a surface by providing on the surface a liquid slurry composition comprising abrasive particles; and contacting the surface with a polishing pad comprising a polymeric matrix and solid lubricant particles.

Other objects and advantages of the present invention will become readily apparent by those skilled in the art from the following detailed description, wherein it is shown and described preferred embodiments of the invention, simply by way of illustration of the best mode contemplated of carrying out the invention. As will be realized the invention is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, without departing from the invention. Accordingly, the description is to be regarded as illustrative in nature and not as restrictive.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a illustrates a shallow trench isolation (STI) structure before planarization.

Figure 1b illustrates the structure after planarization with high topological selectivity i.e. material is removed from the “up” area but not from the “down” area until it becomes level with the up area leading to perfect planarization.

Figure 1b<sup>1</sup> illustrates “dishing” which results in case of low topological selectivity, when material is removed from the down area before it becomes level with the up area.

Figure 2 shows a patterned surface having up and down areas during planarization when

- a. the pad does not touch the wafer referred to as hydrodynamic polishing (Fig. 2a) and
- b. when it does touch the wafer including the bottom surface of the down area. (Fig. 2b). Wafers are upside down during planarization.

Figure 3 illustrates the cross-section of a planarizing/polishing pad according to the present invention showing uniformly distributed solid lubricant particles in a porous pad.

Figure 4 illustrates the cross-section of a planarizing/polishing pad according to the present invention showing uniformly distributed solid lubricant particles in a non-porous pad with micro and macro channels on the surface.

#### BEST AND VARIOUS MODES FOR CARRYING OUT INVENTION

According to the present invention a planarizing/polishing pad that contains solid lubricant particles is provided. The solid lubricant particles enhance the topological selectivity of the planarizing pad. In addition, by reducing the friction between pad and wafer the occurrence of thin film delamination and scratching is reduced. Examples of suitable solid lubricants are organic fluoropolymers such as poly (tetrafluoroethylene) (PTFE); fluoroethylene-propylene copolymers (FEP), perfluoroalkoxy resins (PFA), ethylene-chlorotrifluoroethylene alternating copolymer (ECTFE) and polyvinylidene fluoride (PVDF). Mixtures of solid lubricant particles can be employed, if desired.

The most preferred lubricants are virgin polytetrafluoroethylene particles. Polytetrafluoroethylene is preferred because of its very low coefficient of friction (0.03-0.1) and its chemical inertness. The lubricant particles typically have a coefficient of friction of about 0.3 or below and more typically about 0.03 to about 0.3, and even more typically about 0.03 to about 0.1.

The lubricant particles may have a spherical shape, or cylindrical shape or may contain cut fibers or platelets, the most preferred shape being a spherical shape. The size of the lubricant particles is typically from about 0.05 to about 18 microns, more typically about 0.05 to about 0.5 micron. A typical average particle size is 0.2 micron.

The organic fluoropolymers typically have a weight average molecular weight about  $1 \times 10^5$  to about  $5 \times 10^5$ , and more typically about  $2 \times 10^5$  to about  $3 \times 10^5$ .

The solid lubricant particles may be treated with a surfactant so that if they become detached from the pad in the course of planarization, they may become dispersed in the planarizing slurry. The surfactant, when present, is typically anionic or nonionic. Specific examples of surfactants can be determined by those of ordinary skill in the art once aware of this disclosure and need not be discussed to any further extent in this application.

If it is desired that the solid lubricant particles are bonded to the pad material, adhesion to fluoropolymers can be enhanced by electrochemical treatment as disclosed by US Patent 5,800,858 to Bickford et al. or chemical etch such as TetraEtch® (W.L. Gore and Associates). Such treatment may be followed by the application of a coupling agent, or a coupling agent maybe used without adhesion promotion. Suitable coupling agents include bifunctional coupling agents such as compounds containing a silyl group with either an amine or epoxy group or both and further a fluorinated hydrocarbon group. An example of a silylating coupling agent is N-methyl-N-trimethylsilyltrifluoroacetamide,  $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)\text{COCF}_3$ .

The pads in which the solid lubricant particles can be employed include any of the various types of polishing pad typically made available for the microelectronics industry and typically comprise a polymeric matrix. Examples of suitable matrix materials are polyurethanes including polyester and polyether urethanes, polycarbonates, polyamide, polysulfone, polyvinyl chloride, polyacrylates, polymethacrylates, polyvinylalcohol, polyester, polyacrylamide, polyaramides, epoxies and derivatives of epoxies, and combinations of these polymers. The polymeric matrix can be solid or porous. Examples of pads that can be modified with the solid lubricant particles according to the present invention are those disclosed in US Patents 4,927,432 to Budinger et al., 5,900,164 to Budinger et al. and 5,489,233 to Cook et al; U.S. Patent applications USSN 09/715,184 to Chen et al. and US Patent application USSN 09/668,142, to Chen et al., disclosures of which are incorporated herein by reference.

The amount of solid lubricant particles is typically about 0.5% by weight to about 30% by weight, more typically about 0.5% to about 10% by weight and even more typically about 2 to about 3% by weight, based upon the total weight of the pad.

Polishing pads may be made of a uniform material such as polyurethane or nonwoven fibers impregnated with a synthetic resin binder, or may be formed from multilayer laminations having non-uniform physical properties throughout the thickness of the pad.

A typical laminated pad may have a plurality of layers, such as a spongy and resilient microporous polyurethane layer laminated onto a firm but resilient supporting layer comprising a porous polyester felt with a polyurethane binder. Polishing pads typically may have a thickness in the range of 50-80 mils, preferably about 55 mils, and a diameter in the range of 10 to 36 inches, typically 22.5 inches to polish 200 mm diameter wafers and 29.15 inches to polish 300 mm wafers. Alternatively, the polishing pads may have belt type geometry.

To facilitate, slurry transport, polishing pads also may have macrotextured work surfaces made by surface machining using various techniques. Polishing pads typically may also have microtextured surfaces created by conditioning the pads between wafers.

The pads are typically formed by adding solid lubricant particles to the polymer such as a polyurethane along with auxiliary agents such as surfactants, dispersants, stabilizing agents and polymeric microspheres.

The composition is placed in a mold and cured to form the pad material. If desired, it can then be sliced or dice cut into the desired size and shape and finally buffed.

The reagents that form the polyurethane or the resin binder also may be reacted within a cylindrical container. After forming, a cylindrically shaped piece of pad material is cut into slices that are subsequently used as the polishing pad.

The present pads offer a versatility of properties and performance required to give a high degree of planarization and global uniformity to a variety of polished substrates. The



pads of the present invention can be used for polishing aluminum and aluminum alloys such as Al-Si and Al-Cu, Cu, Cu alloys, Ag, Ag-alloys, Au, Au alloys, W, W alloys, a variety of adhesion and diffusion barriers such as Ti, Ti alloys, TiN, Ta, Ta alloys, TaN, Cr and the like, silicon oxide, polysilicon, silicon nitride, as well as other metals and alloys, and glasses of various compositions.

The present pads are particularly important to polish metal conductors, liners and diffusion barriers when in conjunction with low-k (dielectric constant ) insulators representing delicate structures including air bridges, or planarizing these insulators themselves. Some low-k materials are CVD carbon-doped silicon oxide, such as Black Diamond <sup>TM</sup>, Coral <sup>TM</sup>, SiCOH, their porous versions such as Black Diamond II and Black Diamond III; porous and non-porous spin-on organo silicates JSR 5109, 5117 and the like, and other varieties, such as Shipley Zircon <sup>TM</sup>, Nanoglass; porous and non-porous organic spin-on polymers such as SILK <sup>TM</sup> and porous SILK <sup>TM</sup>. A low friction pad is imperative for polishing such future structures.

The polishing slurries employed can be any suitable CMP slurries. The slurries typically contain abrasive particles such as alumina, ceria, silica, titania, zirconia, polymer particles, organic/inorganic composite particles or combinations thereof. The abrasives typically have a particle size of about 30 to about 1000 nanometers and preferably about 75 to about 300 nanometers.

The amount of abrasive particles is typically about 0.1 to about 20 percent by weight and more typically about 0.3 to about 2 percent of weight.

The slurry can include other ingredients in addition to the abrasive, solid lubricant particles and surfactants such as oxidizing agents, preservatives, anticorrosion agents and the like.

Suitable polishing slurries that contain solid lubricant particles are disclosed in US patent applications 10/295,836 to Ronay, disclosure of which is incorporated herein by reference.

An advantage of the present invention as compared to including solid lubricant particles in the slurry is that the friction of the process can be smaller than with slurries because larger amounts of solid lubricant particles can be incorporated into the pad material then into the slurry without reducing the removal rate to non-economical values.

An embodiment of a pad, suitable for the semiconductor industry, is a substantially cylindrical pad having general dimensions such that it might be used in a polishing apparatus, for example in the equipment described in the IBM Technical Disclosure Bulletin, Vol. 15, No. 6, November 1972, pages 1760-1761, the entire contents of which are incorporated herein by reference.

The parameters of the polishing or planarizing can be determined by those skilled in the art, once aware of this disclosure, without exercising undue experimentation. For instance, the speed of rotation of the polishing pads and also of the wafer is about 10 to about 150 rpm and pressure about 2 to 10 psi. A wafer may be in the range of 100 to 300 mm in diameter.

The following non-limiting Examples are presented to further illustrate the present invention.

#### EXAMPLE 1

A porous polyurethane pad is provided according to the method in U.S. Patent 5,900,164 by mixing liquid urethane with a polyfunctional amine at a proper temperature in the ratio required by the desired amount of cross-linking. During the "low viscosity window" hollow elastic polymeric microspheres are blended with the polymers mixture and 2% by weight of PTFE solid lubricant particles of 0.2 micron average diameter available under the trade name of Pinnacle 9003 by Carroll Scientific Inc., are blended applying a high shear rate mixer. The solid lubricant particles can be added to the liquid urethane or the liquid urethane-polyfunctional amine mixture, or the liquid urethane- polyfunctional amine-microspheres mixture.

The mixture is transferred during the low viscosity window to a convention mold and permitted to gel. It is subsequently cured in an oven, cooled and cut to form polishing pads. Figure 3 shows the cross-section of a planarizing pad according to the present invention showing uniformly distributed solid lubricant particles in the porous pad. The surface of the pad may be supplied with a micro-texture or a macro-texture as described in the above referenced patent in order to facilitate slurry transport during planarization.

In figure 3, numeral 10 represents the polymer matrix, numeral 12, solid lubricant particles, numeral 14, micropores and numeral 16, the surface of the pad.

## EXAMPLE 2

In producing a non-porous pad the process of Example 1 is followed except that the hollow microspheres are not added. Thus a liquid urethane is mixed with a polyfunctional amine at a proper temperature in a ratio required by the desired amount of cross-linking. During the "low viscosity window" 3% by weight of PTFE solid lubricant particles of 0.2 micron average diameter with the trade name of Pinnacle 9003 by Carroll Scientific Inc. are blended into the liquid polymer mix applying a high shear rate mixer. The lubricant particles can be added into the liquid urethane, or into the liquid urethane-polyfunctional amine mixture.

The mixture is transferred during the low viscosity window to a conventional mold and permitted to gel. It is subsequently cured in an oven, cooled and cut to form a polishing pad. Since this pad does not transport slurry well a surface texture providing macroscopic channels for slurry transport is mechanically produced on the surface of the pad before use as given in U.S. Patent 5,489,233, which should be consulted for specifics. In addition a microtexture, produced on the surface of the pad by abrasion at regular intervals during the use of the pad is also claimed in the above patent. Figure 4 shows a non-porous pad with microscopic (20) and macroscopic (18) flow channels containing solid lubricant particles (12) according to the present invention. Numeral 10 represents the polymer matrix and numeral 16 the surface of the pad.

The foregoing description of the invention illustrates and describes only the preferred embodiments of the present invention. However, as mentioned above, it is to be understood that the invention is capable of being made and used in various other combinations, modifications, and environments, and is capable of being changed or modified within the scope of the inventive concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of persons skilled in the relevant art. The embodiments described hereinabove are further intended to explain the best modes known of practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with the various modifications required by the particular applications or uses of the invention. Accordingly, the description is not intended to limit the invention to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

All publications and patent applications cited in this specification are herein incorporated by reference as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference.